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(54) Abstract Title

Barrier coatings

(57) A method of reducing the gas-permeability of a substrate comprises applying a barrier coating of a first polymer to the substrate, and then applying a protective coating of a second polymer to the barrier-coated substrate. The substrate may be a film for shrink-wrapping, a bottle, gasoline tank or paint can, or a preform which is expanded by blow moulding, after applying the coatings, to become oriented. The barrier coating may be polyvinyl alcohol, ethylene-polyvinyl alcohol copolymer or polyvinylidene chloride, of thickness 1-5  $\mu$ m. The protective coating may be a solution of a second polymer of molecular weight 5,000 - 50,000.

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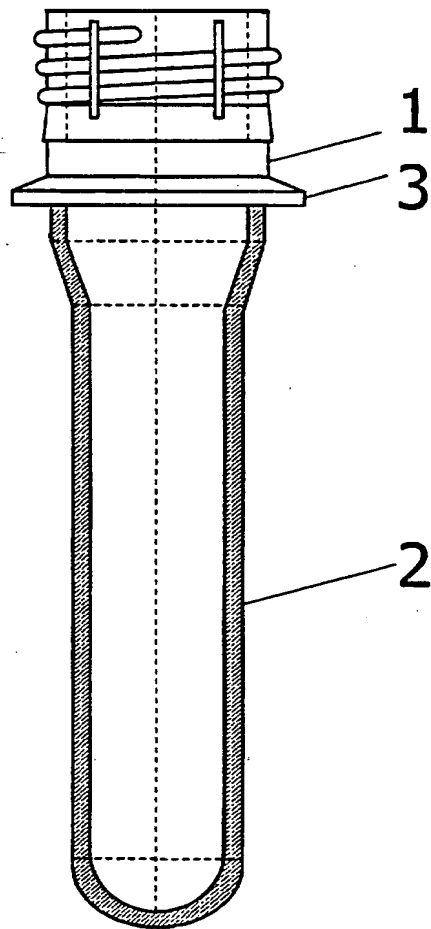


FIGURE 1

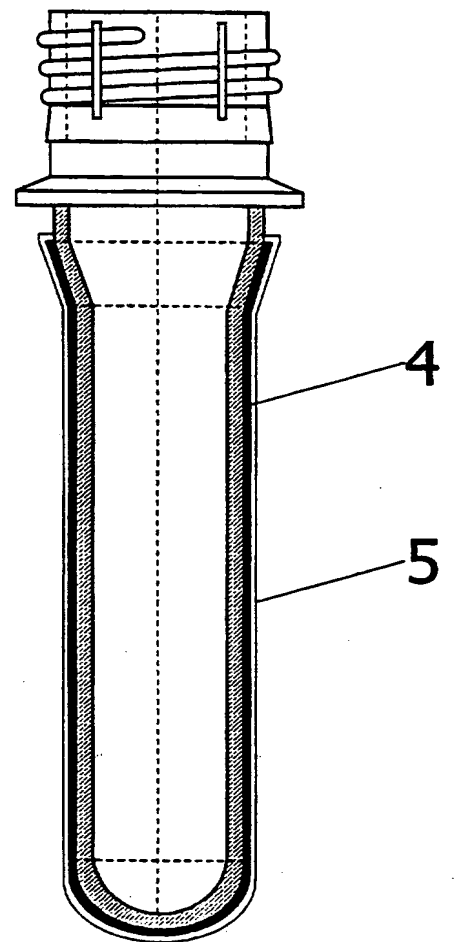


FIGURE 2

## BARRIER COATINGS AND METHODS FOR MANUFACTURING THE SAME

- 5 The present invention relates to barrier coatings and to methods for their manufacture. In particular, the present invention relates to barrier coatings for use in films and containers, which have reduced permeability to oxygen and carbon dioxide and are particularly suitable for use in the food industry.
- 10 Ever increasing demand for consumer products has led to a need for alternative packaging materials. This is especially true in the food industry where conventional packaging materials, such as glass bottles, are often relatively expensive and, from an environmental perspective, difficult to dispose of. In recent years, for example, the use of multilayer packaging
- 15 materials based on high barrier resins has become increasingly important. Drinks supplied in plastic bottles, such as beer and the like, are affected by the presence of air, which leads to oxidation and deterioration of the product and, therefore, to a reduction in shelf-life. Moreover, carbonated soft drinks, as well as beer, are also affected by the loss of carbon dioxide, which leads to a
- 20 flat drink and so reduces shelf-life yet further. The rate of oxidation depends upon the amount of oxygen coming into contact with the product and is less per unit volume of product the larger the bottle. This is because the ratio of the surface area of the bottle to the volume of the product decreases as the bottle size increases. Similarly, the same applies to the rate of loss of carbon
- 25 dioxide through the bottle wall. When packing these products in PET or polyethylene terephthalate bottles, therefore, beer is generally packed in 2 or 3 litre bottles and soft drinks are generally not packed in containers of less than 0.5 litres, with the latter having a shorter shelf-life as a result. Various attempts have been made and continue to be made to improve upon the gas
- 30 transmission rates of plastic bottles made from PET and other polymers.

In the case of beer, conventional procedures involve the use of PET bottles,

which have been coated with polyvinylidenedichloride (PVDC). However, this approach has many disadvantages, including the cost of coating the bottles, the environmental aspect of disposing of chlorinated organic polymers, and the production problems associated with coating "blown" bottles, i.e., bottles that have already been blow-moulded from preforms. In order to address the latter problem, attempts have been made in the past to coat preforms with a single layer of PVDC, prior to blowing the bottles. It was found, however, that the PVDC did not retain its gas barrier properties as the layer got thinner on expansion and minute cracks appeared in the wall of the coating, which therefore led to this technology being abandoned. In an alternative strategy, attempts have also been made to coat blown bottles with polyvinylalcohol (PVOH) or ethylene-vinylalcohol copolymer but it has been found that such coatings suffer from poor adhesion of the coating resins to the bottle walls and from lack of resistance to moisture, thus rendering them unsuitable for most applications.

Another route currently being followed is the production of multilayer bottles by co-extrusion techniques, in which the bottle wall is effectively divided into two sheets with a third layer of a different material inserted between to form a "sandwich". One such bottle is produced by Pechiney, who manufacture a multilayer bottle consisting of PET/EVOH/PET by co-extrusion, where EVOH stands for ethylene vinyl alcohol copolymer having high gas barrier properties. Schmalbach Lubeca also produce a co-extruded multilayer bottle using an aromatic nylon intermediate layer instead of EVOH, which appears to have somewhat inferior barrier properties to EVOH. Cott Corporation is following a similar patch to Schmalbach but is using a nylon intermediate layer, which has even lower barrier properties than the aromatic nylon. However, all of these co-extruded multilayer bottles suffer from a number of disadvantages, in that the cost of the equipment required for co-extrusion of the different polymer layers is very high and the gas barrier levels attained are not sufficient to give the same shelf-life as glass bottles. It is an object of the present invention to overcome some of the aforementioned disadvantages.

Accordingly, in a first aspect of the invention, there is provided a method of reducing the gas-permeability of a substrate, which comprises the steps of applying a barrier coating of a first polymer to the substrate, and then applying a protective coating of a second polymer to the barrier-coated  
5 substrate.

In a second aspect of the invention, there is provided a method of forming an article having reduced gas-permeability, which comprises the steps of applying a barrier coating of a first polymer to a preform, applying a protective coating  
10 of a second polymer to the barrier-coated preform, and expanding the protective-coated preform to obtain the article.

In a third aspect of the invention, there is provided a substrate or an article obtained by a method according to the invention in its first or second aspects.  
15

In a fourth aspect of the invention, there is provided a substrate or an article having a barrier coating of a first polymer on a surface of said substrate or said article and a protective coating of a second polymer overlaid on said barrier coating.  
20

In a fifth aspect of the invention, there is provided a preform having a barrier coating of a first polymer on a surface of said substrate or said article and a protective coating of a second polymer overlying said barrier coating.

25 In a sixth aspect of the invention, there is provided a preform having a barrier coating of polyvinylalcohol or ethylene-polyvinylalcohol copolymer and, optionally, a protective coating of a second polymer overlying said barrier coating.

30 In a seventh aspect of the invention, there is provided a plastic bottle having a barrier coating of polyvinylalcohol at a thickness of between 1 to 5  $\mu\text{m}$ , and a protective coating of a second polymer overlying said barrier coating.

In an eighth aspect of the invention, there is provided a film for shrink warpping having a barrier coating of polyvinylalcohol at a thickness of between 1 to 5  $\mu\text{m}$ , and a protective coating of a second polymer overlying said barrier coating.

5

Preferred embodiments of the invention in any of its various aspects are as described below or as defined in the sub-claims.

The present invention is based upon coating technology and, therefore, does not require the use of highly complex and expensive machinery, such as that needed for co-extrusion processes. Consequently, the inventive processes are particularly suitable for providing barrier coatings on articles having non-uniform or irregular shapes, such as bottles. The barrier coatings may be formed of any suitable materials having the desired gas-permeability characteristics. In a preferred embodiment, the barrier coatings are formed of PVOH or EVOH. However, the invention is not limited to the use of such materials and the underlying principles apply equally to all barrier coatings, including PVDC coatings. The barrier coatings may be dissolved in any suitable solvents but the use of aqueous or aqueous alcoholic solvents is especially preferred. Suitable solvent systems are described in the "EVOH Solution Coated PET Bottles With Improved Gas Barrier", by Teruo Iwanami *et al.*, as presented at FUTURE-PAK '85: Third International Ryder Conference on Packaging Innovation, December 2-4, 1985.

25 The protective coating can be formed of any suitable material, such as PET, polyesters and co-polymers of polyesters, polycarbonate, PEN, PVC, polyolefins, polyamide, polypropylene, polystyrene, aliphatic polyketones, polyethylene, and other resins. Of these, though, PET and copolymers of polyesters are especially preferred, although polycarbonates are also equally good. In a preferred embodiment, high molecular weight co-polyester resins, such as ES100, which is available from Sunkong Industries of Korea, or Vylon 200, which is available from Toyobo Co. Ltd. of Japan, are used. ES100 has

an intrinsic viscosity of 0.62, a softening point of 140°C, a glass transition temperature of 65°C and a molecular weight of 18,000 to 23,000 (MW:GPC). Vylon 200 has an intrinsic viscosity of 0.53, a softening point of 163°C, a glass transition temperature of 67°C and a molecular weight of 15,000 to 20,000. However, other polymers having similar properties, such as, for example, a glass transition temperature in the range of 50 to 75°C, a softening point of between about 120 and 180°C, an intrinsic viscosity of between about 0.40 and 0.80 and a molecular weight of between about 5,000 and 50,000 may also be used. Suitable solvents systems for the protective coating will depend upon the particular polymer used but are well known in the art, although the conditions required to bring high molecular weight resins into solution are not trivial. It has been found that the most effective way of achieving this is generally to dissolve the polymer in the solvent at a temperature close to the boiling point of the solvent by agitating the mixture extremely vigorously at that temperature for at least 24 hours. In the case of PET, a solvent system comprising 90% ethylacetate/10% isopropyl acetate is especially preferred, although for certain co-polyester resins, 100% ethylacetate is very effective. For polycarbonate resins, the use of methylene chloride is generally preferred. Preferably, the protective coating solution comprises about 10 to 40% by weight of the second polymer in the solvent system, particularly about 20% by weight.

In one embodiment, the substrate on which the barrier coating is applied is made of the same material as the protective coating, thus producing a coated substrate having a sandwich structure. Typical constructions include: PET preform/PVOH or EVOH/PET overcoat; PET/PEN blend preform/PVOH or EVOH/PEN overcoat; polycarbonate preform/PVOH or EVOH/polycarbonate overcoat. However, a whole host of combinations is possible and can be adapted to suit various requirements. Similarly, the coating weight of either coating can be altered to suit and, in particular, the nature of the barrier coating to achieve the desired characteristics.

All PET, PEN, polycarbonate bottles, and other bottles are made by first producing a preform or parison, the main body portion of which is then selectively blown into a bottle whilst the neckring is not blown. This can be done in a single stage process, in which the same machine produces a preform and then goes on to blow a bottle, or the production can be split into two stages, in which the preform is first produced on one machine and is then blown as a bottle on another machine. The advantage of the latter process is that it allows preforms having relatively low bulk to be produced at one location and easily transported to a different location, where the final bottles may be blown. In a preferred embodiment, the inventive method involves coating a preform with a barrier coating and then protecting the barrier-coated preform by applying a second coat of another material. Preferably, the coatings are readily stretchable by normal blow-moulding process. It is thought that the outer coating carries the barrier coating with it as a support during the blowing process so that the barrier coat is evenly stretched, thus permitting the use of compounds such as PVDC in the inventive process without attendant cracking.

In a further embodiment of the invention, adhesion of any of coatings to each other and to the substrate is improved by pre-treating the recipient surface of the substrate or the barrier-coated substrate, prior to application of the subsequent coating. Preferably, the recipient surface is heated. In another embodiment, the recipient surface may be treated with an adhesive, such as Cymel or a polyester-based adhesive prior to application of the subsequent coating layer. In a variant of this last embodiment, the adhesive may be mixed, for example, with the barrier coating polymer to improve its adhesion to the substrate. For example, adding 1% by weight of methoxymethylmethylol melamine (Cymel) to PVOH makes its adhesion to other substrates much better and, thus, eliminates or reduces problems of delamination and blistering of the coating. Additional improvement of adhesion may be achieved by flame treatment or corona discharge treatment of the substrate or preform surface prior to application of the coating. The use of such adhesives



can often eliminate the need for a primer, whilst the addition of Cymel to the outer PET coating achieves the same effect.

PVOH or EVOH are especially preferred as barrier coatings, particularly on preforms, because these materials have a great capacity for expansion, without significant loss of gas-permeability properties, possibly as a result of orientation of the molten material during the blowing process. Typically, a coating weight of 0.3 g of PVOH would result in a finished weight of 3 g coating on the finished bottle, which achieves a high gas barrier. A coating weight of 0.5 g of PVOH would achieve a very high barrier. The following tables give an indication of the gas barrier properties achieved by the coating methods according to the invention and by conventional co-extrusion methods:-

Oxygen transmission rate measured in  $\text{cm}^3/\text{m}^2/\text{day}$  @  $23^\circ\text{C}$  and 75% Relative Humidity (RH)

<u>Coated Films</u>		<u>Co-extruded Film</u>	
12 PET/PVOH 1.5 $\mu\text{m}$	0.33	PE/EVOH 2 $\mu\text{m}$ /PE	20
12 OPA/PVOH 1.5 $\mu\text{m}$	0.31	PE/EVOH 5 $\mu\text{m}$ /PE	20
OPP 20/PVOH 1.5 $\mu\text{m}$	3.2	PE/EVOH 12 $\mu\text{m}$ /PE	3

From the above, it can be seen that the barrier coatings prepared according to the invention have superior properties to those produced by conventional co-extrusion methods. In the inventive method, application of a thin coating on a preform and subsequent stretching of this coating to ten times its size means that the final coating of PVOH on the bottle is very thin, typically, in the order of 1-2  $\mu\text{m}$  thick. In normal circumstances, such a thickness might not provide so good a barrier. During the blowing process, it is believed that the PVOH layer becomes oriented, thus improving its gas barrier properties.

Typical oxygen transmission rates for various structures are as follows:-

Oxygen transmission rate measured in  $\text{cm}^3 / \text{m}^2 / \text{day}$  @  $23^\circ\text{C}$  at 75% RH

$\text{CO}_2$  transmission rate measured per  $\text{m}^2$  per day @  $23^\circ\text{C}$  at 50% RH

5 [O<sub>2</sub> and CO<sub>2</sub> transmission rates measured using label panel element of bottle.]

	<u>O<sub>2</sub> transmission</u>	<u>CO<sub>2</sub> Transmission</u>
Standard 2 litre bottle	26	85 (estimated)
10 2 litre preform coated with PVOH, final thickness of PVOH on blown bottle 1.5 $\mu\text{m}$	5.6	2.64
15 2 litre preform coated with PVOH, final thickness of PVOH on blown bottle 2.5 $\mu\text{m}$	4	
20 PVDC/PVOH/PVDC coated preform, blown to 2 litre		
Pechiney 33 cl Bass multilayer EVOH (40 $\mu\text{m}$ ) bottle	4.1	14 (estimated)
25 PVDC coated 2 litre bottle ex Constar	2.9	7 (estimated)

From the above, it can be seen that the O<sub>2</sub> and CO<sub>2</sub> barrier properties of the bottles prepared according to the invention are as good as those obtained by more complex and more expensive co-extrusion technology bottles.

If desired, the protective coating on bottles or films may also be coloured to achieve various decorative effects, for example, the coating can be coloured,

pearlised, frosted, striped and so on. Also multiple layers of the barrier coating can be applied for greater barrier protection. In a preferred embodiment, additional alternate layers of the barrier coating and the protective coating are applied to a substrate, an article or a preform to  
5 provide enhanced rigidity and greater impermeability. In this last embodiment, for example, a typical composition might be: PET preform/PVOH/PET overcoat/PVOH/PET overcoat. In another embodiment, at least one additional barrier coating of a third polymer is applied to the barrier-coated substrate, prior to application of the protective  
10 coating. The third polymer may be the same as the first polymer or may be different. In such an embodiment, for example, typical compositions might be: PET preform/PVDC/PVOH/PVDC/PET overcoat; PET preform/PVDC/PVOH/PVDC; PET preform/PVOH/PVDC/PET overcoat. As will be readily appreciated, however, many other combinations of barrier  
15 coating and protective coating are possible, leading to an almost infinite number of coated substrates.

In order that the invention may be more fully understood, it will now be described, by way of illustration only, with reference to the following  
20 examples, wherein:

Figure 1 shows a conventional preform of a plastic bottle; and

Figure 2 shows the preform of Figure 1 after application of a barrier coating  
25 in accordance with the invention.

In Figures 1 and 2, preform 1 has a main body portion 2 and a neckring 3. A barrier coating 4, consisting of PVOH in 45% water/45% isopropanol/10% methanoic acid, was applied to the mainbody portion 3 of preform 1,  
30 followed by a protective coating of PET. The protective coating was applied in the form of a 20% by weight solution of PET in ethyl acetate which was prepared in the following manner.

80% by weight of ethyl acetate was decanted into a mixing vessel fitted with standard return condensers. The ethyl acetate was heated to a temperature of 75°C whilst being stirred very vigorously with two stirrer motors, each having a rotational speed in excess of 3000 rpm. PET was introduced into the  
5 reaction vessel slowly, so that the stirrers continued to rotate unhindered, and the resultant mixture was left to stir for 24 hours at 75°C. The mixture was then used to coat the PVOH coated preform. 2L bottles were blown from the double coated preforms and the following tests were carried out:-

#### 10 Satra Rub test

Satra is The Shoe & Allied Trades Research Association and, originally, this test was used to check the durability of shoe leather surfaces. The test was carried out by rubbing the material with a fibre-type disk mounted on the shaft of a vertically-mounted motor rotating at a speed of around 200 revs per  
15 minute. The fibre disk rested on the material, which was placed on a flat platform, and a 1 kg weight was placed on top of the motor, equivalent to a weight 200 g/cm<sup>2</sup>. The test was run for 1 minute to test the material's resistance to scuffing. The blown bottle passed the test either dry or with filling line lubricant. For interest, the test was left to run for 1 hour and the  
20 bottle wall was still not affected.

#### Tape Test

The purpose of this test was to check the bonding of the coatings to the bottle wall. Generally, the test is carried out using standard "sellotape" and  
25 the much more severe brown Havana vinyl tape. The bottle coating passed both tests satisfactorily.

#### Carbonation Test

The bottles were filled with 4 volumes of carbon dioxide (the highest rate of  
30 carbonation used in the soft drinks industry is 4 volumes which is very fizzy). These carbon dioxide-filled bottles were then placed in an oven at 38°C and left. The coating was observed at 24, 48 and 72 hours and after 7 days. No

lift of coating was evident.

#### Line Lubricant Test

The bottles were immersed in line lubricant foam and left to stand for 7 days  
5 inside a sealed polythene bag before being examined for signs of stress  
cracking in the base of the bottle. No signs of cracking were observed.

It should be understood that the present invention is not limited to the  
foregoing examples but is equally applicable to a whole range of articles and  
10 manufacturing processes.

For example, at present, around 80% of gasoline tanks in Japan are made of  
metal but there is a move to change to plastic (HDPE). In Europe, some 80%  
of gasoline tanks are plastic and in the United States of America some 50% of  
15 tanks are plastic. With an increase in the (OH) content of gasoline, there is a  
tendency for seepage of such molecules through the plastic tank. Regulations  
are being introduced in the United States of America to cut diffusion from  
plastic tanks down to well below current levels. This has led to severe  
pressure on gasoline tank manufacturers to come up with plastic tanks, which  
20 would conform to the new regulations when these come into effect in the  
next few years. The only solution with currently available co-extrusion  
technology would be to construct multilayer tanks out of PE/EVOH/PE,  
which would require very expensive equipment and heavy capital costs.  
The present invention provides an alternative approach by spray coating  
25 existing plastic gasoline tanks with PVOH or EVOH, and then overcoating  
with a thermoplastic such as PET, PC PEN or the like. This would produce  
a very economical solution to the problem and would obviate the necessity to  
invest in very expensive multilayer technology.

30 In the paint industry, there is a move to change from packaging paints in  
metal paint cans to plastic cans but similar gas barrier problems apply, which  
could be readily solved by means of the double coating technology according

to the present invention.

In the food industry, fresh meats, such as chicken portions, are often shrink-wrapped for display to the customer. Normal polyethylene shrink-wrap film  
5 has an oxygen permeability of  $2,500 \text{ cm}^3 \text{ O}_2/\text{m}^2/\text{day}$  at  $23^\circ\text{C}$  and 50% RH, making it unsuitable for such purposes. Conventional shrink-wrap films that are suitable for such uses are either laminated, like BDF film available from W.R. Grace, United States of America, or PVDC coated, thus making them environmentally unfriendly. Clearly, the present invention would also  
10 overcome such problems, for example, by providing double coated PVOH films. Other areas of application are numerous but include plastic car batteries, plastic wine bottles and plastic wine bags, to name but a few.

CLAIMS

- 5 1. A method of reducing the gas-permeability of a substrate, which comprises the steps of applying a barrier coating of a first polymer to the substrate, and then applying a protective coating of a second polymer to the barrier-coated substrate.
- 10 2. A method as claimed in claim 1, wherein the first polymer is selected from the group consisting of polyvinyl alcohol, ethylene-polyvinyl alcohol copolymer and polyvinylidene dichloride.
3. A method as claimed in claims 1 or 2, wherein the second polymer is  
15 selected from the group consisting of PET, polyesters and co-polymers of polyesters, polycarbonates, polyolefins, PEN, polyvinylchloride, polyamides, polypropylene, polystyrene, aliphatic polyketones and polyethylene.
4. A method as claimed in claimed in claims 1, 2 or 3, wherein the second  
20 polymer has a molecular weight of between about 5,000 and 50,000.
5. A method as claimed in claimed in claim 4, wherein the second polymer has a molecular weight of between about 10,000 and 30,000.
- 25 6. A method as claimed in claimed in claim 5, wherein the second polymer has a molecular weight of between about 15,000 and 25,000.
7. A method as claimed in any one of claims 3 to 6, wherein the second polymer has a viscosity of between about 0.40 and 0.80.
- 30 8. A method as claimed in claim 7, wherein the second polymer has a viscosity of between about 0.50 and 0.65.

9. A method as claimed in any one of claims 3 to 8, wherein the second polymer has a softening point of between about 120 and 180°C.

10. A method as claimed in claim 9, wherein the second polymer has a  
5 softening point of between about 140 and 165°C.

11. A method as claimed in any one of claims 3 to 10, wherein the second polymer is selected from the group consisting of PET, polyesters and copolymers of polyesters, and polycarbonates.

10

12. A method as claimed in any one of claims, wherein the protective coating is formed by applying a solution of the second polymer dissolved in a volatile solvent at a temperature close to the solvent's boiling point.

13. A method as claimed in any one of the preceding claims, wherein the  
15 substrate is formed of a natural or synthetic polymer.

14. A method as claimed in claim 13, wherein the protective coating is formed of the same natural or synthetic polymer as the substrate.

20

15. A method as claimed in any one of the preceding claims, wherein the substrate is pre-treated prior to application of the barrier coating in order to promote or improve adherence of the barrier coating.

16. A method as claimed in any one of the preceding claims, wherein the  
25 barrier-coated substrate is pre-treated prior to application of the protective coating in order to promote or improve adherence of the protective coating.

17. A method as claimed in claims 15 or 16, wherein the substrate or  
30 barrier-coated substrate is heated prior to application of the subsequent coating.



18. A method as claimed in claim 17, wherein the substrate or barrier-coated substrate is subjected to flame treatment or corona discharge.
19. A method as claimed in any one of claims 15 to 18, wherein the  
5 substrate or barrier-coated substrate is pre-treated with an adhesive prior to application of the subsequent coating.
20. A method as claimed in any one of the preceding claims, wherein the  
10 barrier coating or the protective coating further comprises an adhesive to promote or improve adhesion of the coating.
21. A method as claimed in claims 19 or 20, wherein the adhesive is a methoxymethylmethyolmelamine or a polyester-based adhesive.
- 15 22. A method as claimed in any one of the preceding claims, wherein the thickness of the barrier coating is in the range of 0.01 to 100  $\mu\text{m}$ , preferably 0.1 to 10  $\mu\text{m}$ , and most preferably 1 to 5  $\mu\text{m}$ .
23. A method as claimed in any one of the preceding claims, wherein at  
20 least one additional barrier coating of a third polymer is applied to the barrier-coated substrate, prior to application of the protective coating.
24. A method as claimed in claim 23, wherein the third polymer and the  
25 first polymer are the same.
25. A method as claimed in any one of the preceding claims, further comprising the step of applying, alternately, at least one additional barrier coating and at least one additional protective coating to the substrate.
- 30 26. A method as claimed in any one of the preceding claims, wherein the coated substrate has an oxygen transmission rate of less than 10  $\text{cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity, preferably less than 5  $\text{cm}^3$ , and most

preferably less than 3 cm<sup>3</sup>.

27. A method as claimed in any one of the preceding claims, wherein the barrier coating or the protective coating are applied to the substrate by spray-coating, dip-coating, roll-coating or any combination thereof.

28. A method of forming an article having reduced gas-permeability by a method according to any one of claims 1 to 27, which comprises the steps of applying a barrier coating of a first polymer to a preform, applying a protective coating of a second polymer to the barrier-coated preform, and expanding the protective-coated preform to obtain the article.

29. A method as claimed in claim 28, wherein the preform is expanded by blow-moulding.

15

30. A method as claimed in claims 28 or 29, wherein the first polymer has a lower glass transition temperature than the second polymer.

31. A method as claimed in claims 28, 29 or 30, wherein the first polymer becomes substantially plastic during expansion.

32. A method as claimed in claim 31, wherein the first polymer becomes orientated during expansion, thereby reducing its gas-permeability.

25 33. A method as claimed in any one of claims 28 to 32, wherein the second polymer supports the first polymer during expansion, thereby ensuring uniform stretching of the first polymer.

34. A method as claimed in claim 33, wherein the first polymer is polyvinylidenedichloride.

30

35. A method of reducing the gas-permeability of a substrate or a method

of forming an article having reduced gas-permeability substantially as hereinbefore described in any of the foregoing examples.

36. A substrate or an article obtained by a method as claimed in any one  
5 of the preceding claims.

37. A substrate or an article having a barrier coating of a first polymer on a surface of said substrate or said article and a protective coating of a second polymer overlaid on said barrier coating.

10

38. A substrate or an article as claimed in claim 37, wherein the first polymer is selected from the group consisting of polyvinyl alcohol, ethylene-polyvinyl alcohol copolymer and polyvinylidene dichloride.

15 39. A substrate or an article as claimed in claims 37 or 38, wherein the second polymer is selected from the group consisting of PET, polyesters and co-polymers of polyesters, polycarbonates, polyolefins, PEN, polyvinylchloride, polyamides, polypropylene, polystyrene, aliphatic polyketones and polyethylene.

20

40. A substrate or an article as claimed in claim 39, wherein the second polymer has a molecular weight of between about 5,000 and 50,000.

25 41. A substrate or an article as claimed in claim 40, wherein the second polymer has a molecular weight of between about 10,000 and 30,000.

42. A substrate or an article as claimed in claim 41, wherein the second polymer has a molecular weight of between about 15,000 and 25,000.

30 43. A substrate or an article as claimed in any one of claims 39 to 42, wherein the second polymer has a viscosity of between about 0.40 and 0.80.

44. A substrate or an article as claimed in claim 43, wherein the second polymer has a viscosity of between about 0.50 and 0.65.

45. A substrate or an article as claimed in any one of claims 39 to 44,  
5 wherein the second polymer has a softening point of between about 120 and 180°C.

46. A substrate or an article as claimed in claim 45, wherein the second polymer has a softening point of between about 140 and 165°C.

10

47. A method as claimed in any one of claims 39 to 46, wherein the second polymer is selected from the group consisting of PET, polyesters and copolymers of polyesters, and polycarbonates.

15 48. A substrate or an article as claimed in any one of claims 37 to 47, wherein the substrate is formed of a natural or synthetic polymer.

49. A substrate or an article as claimed in claim 48, wherein the protective coating is formed of the same natural or synthetic polymer as the substrate.

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50. A substrate or an article as claimed in any one of claims 37 to 49, wherein the thickness of the barrier coating is in the range of 0.01 to 100  $\mu\text{m}$ , preferably 0.1 to 10  $\mu\text{m}$ , and most preferably 1 to 5  $\mu\text{m}$ .

25 51. A substrate or an article as claimed in any one of claims 37 to 50, wherein the coated substrate has an oxygen transmission rate of less than 10  $\text{cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity, preferably less than 5  $\text{cm}^3$ , and most preferably less than 3  $\text{cm}^3$ .

30 52. A substrate or an article as claimed in any one of claims 37 to 51 being a barrier film, a preform or a container.

53. An article as claimed 52, wherein the container is a bottle, a gasoline tank or a paint can.

54. A substrate or an article substantially as hereinbefore described in any  
5 of the foregoing examples.

55. A preform having a barrier coating of a first polymer on a surface of said substrate or said article and a protective coating of a second polymer overlying said barrier coating.

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56. A preform having a barrier coating of polyvinylalcohol or ethylene-polyvinylalcohol copolymer and, optionally, a protective coating of a second polymer overlying said barrier coating.

15 57. A plastic bottle having a barrier coating of polyvinylalcohol at a thickness of between 1 to 5  $\mu\text{m}$ , and a protective coating of a second polymer overlying said barrier coating.

58. A film suitable for shrink wrapping having a barrier coating of  
20 polyvinylalcohol at a thickness of between 1 to 5  $\mu\text{m}$ , and a protective coating of a second polymer overlying said barrier coating.

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**Amendments to the claims have been filed as follows**

- 5 1. A method of reducing the gas-permeability of a substrate, which comprises the steps of applying a barrier coating of a first polymer to the substrate, and then applying a solution of a second polymer having a molecular weight of between about 5,000 and 50,000 to the barrier-coated substrate to form a protective coating.
- 10 2. A method as claimed in claim 1, wherein the first polymer is selected from the group consisting of polyvinyl alcohol, ethylene-polyvinyl alcohol copolymer and polyvinylidene dichloride.
- 15 3. A method as claimed in claims 1 or 2, wherein the second polymer is selected from the group consisting of polyesters and co-polymers of polyesters, polycarbonates, polyolefins, polyvinylchloride, polyamides and aliphatic polyketones.
- 20 4. A method as claimed in claim 3, wherein the second polymer is selected from the group consisting of polyesters and copolymers of polyesters, and polycarbonates.
- 25 5. A method as claimed in claim 3, wherein the second polymer is selected from the group consisting of polyethylene terephthalate, polyethylene naphthalate, polyethylene, polypropylene and polystyrene.
6. A method as claimed in any one of the preceding claims, wherein the second polymer has a molecular weight of between about 10,000 and 30,000.
- 30 7. A method as claimed in claim 6, wherein the second polymer has a molecular weight of between about 15,000 and 25,000.

8. A method as claimed in any one of claims 3 to 7, wherein the second polymer has a viscosity of between about 0.40 and 0.80.
9. A method as claimed in claim 8, wherein the second polymer has a viscosity of between about 0.50 and 0.65.
10. A method as claimed in any one of claims 3 to 9, wherein the second polymer has a softening point of between about 120 and 180°C.
11. A method as claimed in claim 10, wherein the second polymer has a softening point of between about 140 and 165°C.
12. A method as claimed in any one of the preceding claims, wherein the protective coating is formed by applying a solution of the second polymer dissolved in a volatile solvent at a temperature close to the solvent's boiling point.
13. A method as claimed in any one of the preceding claims, wherein the substrate is formed of a natural or synthetic polymer.
14. A method as claimed in claim 13, wherein the protective coating is formed of the same natural or synthetic polymer as the substrate.
15. A method as claimed in any one of the preceding claims, wherein the substrate is pre-treated prior to application of the barrier coating in order to promote or improve adherence of the barrier coating.
16. A method as claimed in any one of the preceding claims, wherein the barrier-coated substrate is pre-treated prior to application of the protective coating in order to promote or improve adherence of the protective coating.
17. A method as claimed in claims 15 or 16, wherein the substrate or

barrier-coated substrate is heated prior to application of the subsequent coating.

18. A method as claimed in claim 17, wherein the substrate or barrier-coated substrate is subjected to flame treatment or corona discharge.

19. A method as claimed in any one of claims 15 to 18, wherein the substrate or barrier-coated substrate is pre-treated with an adhesive prior to application of the subsequent coating.

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20. A method as claimed in any one of the preceding claims, wherein the barrier coating or the protective coating further comprises an adhesive to promote or improve adhesion of the coating.

15 21. A method as claimed in claims 19 or 20, wherein the adhesive is a methoxymethylmethyloimelamine or a polyester-based adhesive.

22. A method as claimed in any one of the preceding claims, wherein the thickness of the barrier coating is in the range of 0.01 to 100  $\mu\text{m}$ .

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23. A method as claimed in claim 22, wherein the thickness of the barrier coating is in the range of 0.1 to 10  $\mu\text{m}$ .

24. A method as claimed in claim 23, wherein the thickness of the barrier coating is in the range of 1 to 5  $\mu\text{m}$ .

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25. A method as claimed in any one of the preceding claims, wherein at least one additional barrier coating of a third polymer is applied to the barrier-coated substrate, prior to application of the protective coating.

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26. A method as claimed in claim 25, wherein the third polymer and the first polymer are the same.



27. A method as claimed in any one of the preceding claims, further comprising the step of applying, alternately, at least one additional barrier coating and at least one additional protective coating to the substrate.
28. A method as claimed in any one of the preceding claims, wherein the coated substrate has an oxygen transmission rate of less than  $10 \text{ cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity.
29. A method as claimed in claim 28, wherein the coated substrate has an oxygen transmission rate of less than  $5 \text{ cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity.
30. A method as claimed in claim 29, wherein the coated substrate has an oxygen transmission rate of less than  $3 \text{ cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity.
31. A method as claimed in any one of the preceding claims, wherein the barrier coating or the protective coating are applied to the substrate by spray-coating, dip-coating, roll-coating or any combination thereof.
32. A method of forming an article having reduced gas-permeability by a method according to any one of claims 1 to 31, which comprises the steps of applying a barrier coating of a first polymer to a preform, applying a solution of a second polymer having a molecular weight of between about 5,000 and 50,000 to the barrier-coated preform to form a protective coating, and expanding the protective-coated preform to obtain the article.
33. A method as claimed in claim 32, wherein the preform is expanded by blow-moulding.
34. A method as claimed in claims 32 or 33, wherein the first polymer has a lower glass transition temperature than the second polymer.

35. A method as claimed in claims 32, 33 or 34, wherein the first polymer becomes substantially plastic during expansion.

36. A method as claimed in any one of claims 32 to 35, wherein the first polymer becomes orientated during expansion, thereby reducing its gas-permeability.

37. A method as claimed in any one of claims 32 to 36, wherein the second polymer supports the first polymer during expansion, thereby ensuring uniform stretching of the first polymer.

38. A method as claimed in claim 37, wherein the first polymer is polyvinylidenedichloride.

39. A method of reducing the gas-permeability of a substrate or a method of forming an article having reduced gas-permeability substantially as hereinbefore described in any of the foregoing examples.

40. A substrate or an article obtained by a method as claimed in any one of the preceding claims.

41. A substrate or an article having a barrier coating of a first polymer on a surface of said substrate or said article and a protective coating formed from a solution of a second polymer having a molecular weight of between about 5,000 and 50,000 overlaid on said barrier coating.

42. A substrate or an article as claimed in claims 40 or 41, wherein the first polymer is selected from the group consisting of polyvinyl alcohol, ethylene-polyvinyl alcohol copolymer and polyvinylidene dichloride.

43. A substrate or an article as claimed in claims 40, 41 or 42, wherein the second polymer is selected from the group consisting of polyesters and co-

polymers of polyesters, polycarbonates, polyolefins, polyvinylchloride, polyamides, and aliphatic polyketones.

44. A substrate or an article as claimed in claim 43, wherein the second  
5 polymer is selected from the group consisting of polyesters and copolymers of  
polyesters, and polycarbonates.

45. A substrate or an article as claimed in claim 43, wherein the second  
polymer is selected from the group consisting of polyethylene terephthalate,  
10 polyethylene naphthalate, polyethylene, polypropylene and polystyrene.

46. A substrate or an article as claimed in any one of claims 40 to 45,  
wherein the second polymer has a molecular weight of between about 10,000  
and 30,000.

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47. A substrate or an article as claimed in claim 46, wherein the second  
polymer has a molecular weight of between about 15,000 and 25,000.

48. A substrate or an article as claimed in any one of claims 40 to 47,  
20 wherein the second polymer has a viscosity of between about 0.40 and 0.80.

49. A substrate or an article as claimed in claim 48, wherein the second  
polymer has a viscosity of between about 0.50 and 0.65.

25 50. A substrate or an article as claimed in any one of claims 40 to 49,  
wherein the second polymer has a softening point of between about 120 and  
180°C.

51. A substrate or an article as claimed in claim 50, wherein the second  
30 polymer has a softening point of between about 140 and 165°C.

52. A substrate or an article as claimed in any one of claims 40 to 51,

wherein the substrate is formed of a natural or synthetic polymer.

53. A substrate or an article as claimed in claim 52, wherein the protective coating is formed of the same natural or synthetic polymer as the substrate.

54. A substrate or an article as claimed in any one of claims 40 to 53, wherein the thickness of the barrier coating is in the range of 0.01 to 100  $\mu\text{m}$ .

55. A substrate or an article as claimed in claim 54, wherein the thickness of the barrier coating is in the range of 0.1 to 10  $\mu\text{m}$ .

56. A substrate or an article as claimed in claim 55, wherein the thickness of the barrier coating is in the range of 1 to 5  $\mu\text{m}$ .

57. A substrate or an article as claimed in any one of claims 40 to 56, wherein the coated substrate has an oxygen transmission rate of less than 10  $\text{cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity.

58. A substrate or an article as claimed in any one of claims 40 to 56, wherein the coated substrate has an oxygen transmission rate of less than 5  $\text{cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity.

59. A substrate or an article as claimed in any one of claims 40 to 56, wherein the coated substrate has an oxygen transmission rate of less than 3  $\text{cm}^3/\text{m}^2/\text{day}$  at ambient temperature and humidity.

60. An article as claimed in any one of claims 40 to 59, being a barrier film, a preform or a container.

61. An article as claimed 60, wherein the container is a bottle, a gasoline tank or a paint can.

62. A substrate or an article substantially as hereinbefore described in any of the foregoing examples.

63. A preform comprising a substrate or an article having a barrier coating of a first polymer on a surface of said substrate or said article and a protective coating formed from a solution of a second polymer having a molecular weight of between about 5,000 and 50,000 overlying said barrier coating.

64. A plastic bottle having a barrier coating of polyvinylalcohol at a thickness of between 1 to 5  $\mu\text{m}$ , and a protective coating formed from a solution of a second polymer having a molecular weight of between about 5,000 and 50,000 overlying said barrier coating.

65. A film suitable for shrink wrapping having a barrier coating of polyvinylalcohol at a thickness of between 1 to 5  $\mu\text{m}$ , and a protective coating formed from a solution of a second polymer having a molecular weight of between about 5,000 and 50,000 overlying said barrier coating.



Application No: GB 9816267.0  
Claims searched: 1-55/57-58

Examiner: Richard Kennell  
Date of search: 15 September 1998

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK Cl (Ed.P): B2E (EM)  
Int Cl (Ed.6): B29B 11/14 15/10; B29C 49/22 51/14; B65D 23/02 23/08 65/42  
Other: Online (WPI); Selected publications

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2090219 A (TOYO SEIKAN), whole document	1-3, 11,13,15, 19, 22, 27-29,31- 34, 36-39, 47-50,52, 53,55
X	GB 2014083 A (RHONE-POULENC), whole document, see especially page 3 lines 40-47	1-3,13, 17-19,22, 28,29,31- 33,36-38, 48,50,52, 53,55,57, 58
X,Y	GB 2014082 A (RHONE-POULENC), whole document, see especially page 2 line 99 - page 3 line 3	X-ditto plus 11,14,39, 47,49; Y-4-10/40- 46
X	EP 0254468 A (DU PONT CANADA), whole document, see especially page 5 lines 3-5 and page 6 lines 27-33	1-3,13,15, 19,27,36- 39,48,52

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



Application No: GB 9816267.0  
Claims searched: 1-55/57-58

Examiner: Richard Kennell  
Date of search: 15 September 1998

Category	Identity of document and relevant passage	Relevant to claims
Y	WO 97/01427 A (VALYI), see page 7 line 7 - page 8 line 8	4-8/40-44
Y	US 5628957 A (COLLETTE), see col 2 lines 56-63, col 7 lines 2-19 and col 10 lines 23-27	7-10/43-46
X	US 4731266 A (BONNEBAT), whole document, see especially col 15 line 64 - col 16 line 6	As GB 2014083 A
X	US 4418119 A (MORROW), whole document	1,2,23,24, 36-38,52
X	US 3579371 A (DOOLEY), whole document	1,2,13,27, 36-38,48,52
X	US 3514367 A (JAMES), whole document, see especially col 2 lines 14-64	1-3,15,19, 22-24,36-39,48,50, 52
X	WPI Abstract Accession No 94-192007[24] & AU 9346149 A (GRACE & CO), see abstract	1-3,13-16, 19,20,36-39,48,49, 52,58
Y	"Encyclopedia of Polymer Science and Engineering", ed H F Mark et al, 2nd Edition, vol 12, published 1988 Wiley-Interscience, see "Molecular Weight" at pages 226-227	4-8/40-44

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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